SYNTEX agribusiness inc. NUTRITION AND CHEMICAL DIVISION ENVIRONMENTAL PROJECTS DEPARTMENT

JDB

Site: Syntex Verona
ID # MOD007452154
Area: 2.1
Other: OU#1
3-5-91
3.0

RECEIVED
MAR 06 1991
REMD SECTION

0751

0751

40032236
OU-02 SUPERFUND RECORDS

March 5, 1991

RECEIVED
MAR 11 1991
WASTE MANAGEMENT PROGRAM
MISSOURI DEPARTMENT OF
NATURAL RESOURCES

Mr. Glenn Curtis
U.S. Environmental Protection Agency
Region VII
726 Minnesota Avenue
Kansas City, KS 66101

Re: Verona Fish and Sediment Plan

Dear Glenn:

Enclosed are materials concerning the levels of 2,3,7,8-Tetrachlorodibenzo-p-dioxin ("dioxin") in fish collected from the Spring River downstream from the Syntex Agribusiness, Inc. ("Syntex") plant in Verona, Missouri. As we discussed during our conference call on November 29, 1990, the levels of dioxin found in fish obtained from the Spring River in 1990 are the lowest recorded during the seven years of the project.

The enclosed information is submitted in accordance with: (1) the September 9, 1983 Consent Agreement and Order ("Order") between Syntex and the U.S. Environmental Protection Agency ("EPA"); (2) the Verona Fish and Sediment Plan ("Plan"); and (3) the terms of a one year extension of the sampling and analysis program as expressed in letters between Syntex and EPA dated July 17, 1990 and October 3, 1990. The enclosures include the annual report of fish samples taken from the Spring River in 1990, the statistical analysis of those samples and samples taken in previous years, and a statistical report that summarizes the conclusions drawn from the analysis.

The annual analytical report documents the origins of the samples and the method of analysis, as discussed in the October 3, 1990 memorandum from Dr. Chan et al. to Dr. David Robertson. Table 1 of the report sets out the concentrations of dioxin detected in the fish fillets.

The statistical analysis ("Statistical Analysis of Dioxin Data From Spring River - Statistical Package", dated November 12, 1990) considers the data summarized in the 1990 annual report along with the fish data for Sites 1 and 2 contained in the annual reports for 1984 through 1989. The statistical analysis also considers the 1990 data with data collected since remediation of the Verona plant was initiated in 1987. This is a particular important time frame since the presumed source(s) of dioxin contamination of the Spring River were removed during this remedial effort. Finally, the statistical report, dated December 14, 1990, considers the results of the statistical analysis in light of the criteria set forth in the Order and Plan.

MAILING ADDRESS: P.O. BOX 1246, SPRINGFIELD, MO 65801 • (417) 866-4050 ALTERNATE NO. (417) 866-7291
SHIPPING ADDRESS: 2460 WEST BENNETT, SPRINGFIELD, MO 65807

The Order provides that the initial five year sampling and analysis project may be extended if there is no statistically significant decrease in the fish results at Site 1, or when a statistically significant aggregate increase in the fish results has been observed at all other sampling points. As set forth in more detail in the statistical analysis and report, there has been a significant decrease in the levels of dioxin in fish obtained from Site 1. The data gathered at Site 1 during and after the Verona remedial effort show dramatic decreases in dioxin levels. The Final Progress Report, which discussed the results obtained during the initial five year study, and the 1989 statistical report demonstrated that there has been no statistically significant aggregate increase in the fish results from Sites 2 through 5 and from Sites 2 through 4, respectively. For 1990, the data from Site 2 show dioxin levels in fish fillets that are markedly lower than any of the sampling results from prior years for Site 2. For these and other reasons, the report concludes that further sampling and analysis of Spring River fish is not warranted.

After you and your staff have had an opportunity to review the enclosed information, please contact me so that we may schedule a mutually convenient meeting or telephone conference call.

Sincerely,

SYNTEX AGRIBUSINESS, INC.

Gary J. Pendergrass
By F.L.

Gary J. Pendergrass, P.E.
Manager, Environmental Projects

GJP:rlr/0818P

Enclosures

xc: Morris Kay (w/Encl.)

STATISTICAL REPORT

VERONA FISH AND SEDIMENT PLAN

DECEMBER 14, 1990

by

SYNTEX AGRIBUSINESS, INC.

Statistical Report

This statistical report ("Report") summarizes the conclusions drawn from the annual analytical report of fish samples taken from the Spring River in 1990, and from the Statistical Analysis of Dioxin Data From the Spring River ("statistical analysis"). Specifically, this Report compares the information contained in the annual report and the statistical analysis with the criteria set forth in the September 9, 1983 Consent Agreement and Order ("Order") between Syntex Agribusiness, Inc. ("Syntex") and the U.S. Environmental Protection Agency ("EPA").

This Report and the accompanying annual report and statistical analysis have been developed by Syntex in accordance with the provisions of the Order, the Verona Fish and Sediment Plan ("Plan") developed and approved under the Order, and the terms of a one year extension of the sampling and analysis program as expressed in July 17, 1990 and October 3, 1990 letters between Syntex and EPA. As discussed in the Report, additional sampling and analysis of Spring River fish under the Order is not warranted.

Background

The sampling and analysis of Spring River fish and sediment commenced in 1984 and has continued in several phases to the present time. As explained in more detail below, the initial five years of the project involved fish and sediment sampling from five locations on the Spring River. The sixth year of the project involved only fish sampling and analysis from four of the five locations on the Spring River, and this seventh year encompasses only fish sampling and analysis from two of the five locations on the Spring River.

The project was designed to monitor whether there were statistically significant increases or decreases in the levels of dioxin in the fish and sediment downstream from the Syntex Verona, Missouri, plant. Under the Order and Plan, the sampling and analysis was to extend for an initial five years, with discretionary and non-discretionary options for extending or shortening the five year program under certain specified conditions. Using its discretion under the Order, in light of the annual analytical and statistical results, EPA has progressively cut back on the extent of the sampling program since the end of the initial five year period.

The conditions under which EPA may extend the five year program are set out in paragraph 42 of the Order. Paragraph 42 provides, in part, that:

> "EPA may extend the initial five (5) year period at one year intervals and at twelve (12) mile increments for up to 5 years past this initial sampling period when no statistically significant decrease in the fish results has been observed at the 0.3 mile location downstream...or when a statistically significant aggregate increase in the fish results has been observed at all other sampling points...Sediment sampling...may be extended by EPA at one (1) year intervals and at 12 mile increments if there is a statistically significant increase in sediment results at the

0.3 mile location or a statistically significant aggregate increase in sediment results at all other sampling points."

The Plan establishes a significance level of 0.05 (or 95%) for data pertaining to Site 1.

As provided by the Order and Plan, samples of fish were obtained annually from 1984-1988 from five locations in the Spring River. In accordance with paragraph II of the Plan, fish samples were taken 0.3 miles downstream from the confluence of the Slough Area and the Spring River (Site 1); 3.0 miles downstream (Site 2); 6.0 miles downstream (Site 3); 9.0 miles downstream (Site 4); and 12.0 miles downstream (Site 5). As also provided by the Order and Plan, sediment samples were obtained annually for the five year period from Sites 1, 3, and 5. The fish and sediment samples were collected and analyzed in accordance with the requirements of the Order and Plan, and Syntex submitted to EPA five annual reports containing the yearly results of the Spring River fish and sediment sampling and analysis.

As provided by paragraph 47 of the Order and paragraph VI of the Plan, Syntex prepared a Final Progress Report and Statistical Package, dated January 30, 1989, that assessed the fish and sediment data collected during 1984 through 1988. Based upon the statistical analysis of the data collected over the five year period, the Final Progress Report concluded that:

(1) There was neither a statistically significant decrease nor increase in the levels of dioxin in fish taken from sampling Site 1 over the five year period;

(2) The statistical analysis did not support the hypothesis that there was a statistically significant increase in dioxin levels in the fish taken from sampling Sites 2 through 5 over the five year period;

(3) The statistical analysis did not support the hypothesis that there was a statistically significant increase in dioxin in the sediment taken from Site 1 over the five year period; and

(4) The statistical analysis did not support the hypothesis that there was a statistically significant increase in dioxin in the sediment taken from Sites 3 and 5 over the five year period.

The Final Report emphasized that the levels of dioxin detected in the fish and sediment were extremely low. It pointed out that the dioxin levels found in the fish were actually below the sensitivity of the analytical procedure anticipated by the Plan, and that the dioxin levels were considerably below the advisory levels used by the U.S. Food and Drug Administration.

Considering the purposes of the sampling and analysis program, and the criteria set out in the Order, the Final Report concluded that additional sampling of the fish and sediment was not warranted. However, EPA requested that the program be extended for an additional year to collect and analyze only fish samples from Sites 1 through 4. Syntex agreed to this one year extension and submitted an annual report of the 1989 data on November 27,

1989, and a statistical analysis on February 21, 1990 that assessed the 1989 data in conjunction with the fish data that had been collected for Sites 1 through 4 during 1984 through 1988. Consistent with the criteria established in paragraph 42 of the Order, Syntex organized the data generated over the six year period by considering the fish sampling results at Site 1, and the fish sampling results from Sites 2 through 4. The Statistical Report for the six year period of the project concluded that:

(1) The statistical analysis demonstrated that there was neither a statistically significant decrease nor a statistically significant increase in dioxin levels in fish taken from sampling Site 1 over the six year period; and

(2) The statistical analysis did not support the hypothesis that there was a statistically significant increase in dioxin levels in fish taken from sampling Sites 2 through 4 over the six year period.

Again, EPA requested a one year extension of the sampling program. As reflected in Syntex' October 3, 1990 letter to Mr. Glenn Curtis, Syntex agreed to collect fish from Sites 1 and 2 and to analyze fillets from the fish samples. It is the data generated from the fish collected from Sites 1 and 2 in 1990 that is the subject of this Report and the attached statistical analysis.

Summary of the 1990 Sampling Program and Statistical Analysis

The accompanying statistical analysis was performed on data collected from Sites 1 and 2 during the past seven years, including data collected in 1990. In order to correspond to the criteria in paragraph 42 of the Order quoted above, the dioxin concentrations in fish from Site 1 were tested against the hypothesis of a decrease in dioxin levels with time using both a Jonckheere test and a Student's t (multiple linear regression) test. The resulting p-values were 0.15 and 0.07, respectively, indicating a decreasing trend over time.

The statistical analyses and reports in prior years have not considered Site 2 data separately from the data collected from other downstream Sites, and evaluation criteria for Site 2 alone are not specified in the Order. Paragraph 42 of the Order combines Site 2 with the other downstream Sites and provides that the study may be extended if there is a statistically significant increase in the fish results at these Sites considered in the aggregate. As discussed above, the Final Progress Report and the 1989 Statistical Report demonstrated that this criteria for an extension of the study had not been met at Sites 2 through 5 during the initial five year study, or at Sites 2 through 4 during the sixth year of the study. Considering the data obtained in 1990, Site 2 fish dixon levels are markedly lower than any of the sampling results from prior years for this Site. These results are, in fact, similar to previous Sites 3 and 4 dioxin concentrations which have consistently been only slightly above non-detect levels since 1985 and may represent the background dioxin level for this section of the Spring River.

The data collected in 1990 from Sites 1 and 2 was combined and analyzed for a decrease in dioxin levels over the seven year study using multiple linear regression. The corresponding p-value was 0.06, strong evidence of a decrease in concentration over the seven year sample period.

The statistical analysis also examines the potential impact of the remediation of the Verona plant upon the sampling results. A statistical analysis was performed on data collected from Sites 1 and 2 from 1987 to 1990. The dioxin-contaminated soil from the Verona plant was excavated early in the summer of 1988, before the fish and sediment samples were taken in that year. In spite of decreased power due to the smaller sample size, the results indicate a highly significant decrease in dioxin concentrations over the past four years at Site 1, at Site 2, and at both Sites combined. The resulting p-values were less than 0.05.

Conclusions

The statistical analysis documents the following conclusions concerning levels of dioxin in Spring River fish:

(1) The dioxin concentrations in fish from Site 1 reflect a decreasing trend over the seven year sampling interval. The statistical analysis using the linear regression analysis for Site 1 demonstrated 93% confidence that there is a decrease in dioxin levels in fish taken from sampling Site 1 over the past seven years. The statistical analysis using the Jonckheere test, which is very sensitive to an occasional change in the trend, demonstrated 85% confidence that there is a decrease in dioxin levels in fish taken from sampling Site 1 over the past seven years;

(2) A statistically significant decrease in dioxin levels was observed in fish fillets collected from Site 1 over the last four years following remediation of the Verona plant. The statistical analysis using the linear regression analysis for Site 1 demonstrated greater than 99% confidence that there is a statistically significant decrease in dioxin levels in fish taken from sampling Site 1 over the past four years. The statistical analysis using the Jonckheere test demonstrated 98% confidence that there is a statistically significant decrease in dioxin levels in fish taken from sampling Site 1 over the past four years;

(3) The Final Progress Report and the 1989 Statistical Report demonstrated that there has been no statistically significant increase in dioxin levels from fish taken from Sites 2 through 5, and from Sites 2 through 4, respectively. Site 2 fish dioxin levels in 1990 are markedly lower than any previous data for this Site. These results are similar to previous Site 3 and Site 4 dioxin data and may represent the background dioxin level. The statistical analysis on Site 2 data alone did not support the hypothesis that there was a statistically significant decrease in dioxin levels over the past seven years in fish taken from sampling Site 2. Because this hypothesis is not a criteria set forth in the Order, it is included in this Report for informational purposes only;

(4) A statistically significant decrease, using multiple linear regression, in Site 2 fish dioxin levels has occurred during the four years following the Verona plant remediation. The statistical analysis using the linear regression analysis for Site 2 demonstrated 97% confidence that there is a statistically significant decrease in dioxin levels in fish taken from sampling Site 2 over the past four years. The statistical analysis using the Jonckheere test demonstrated 90% confidence that there is a decrease in dioxin levels in fish taken from sampling Site 2 over the past four years. For the reasons stated in item (3) above, this conclusion is included for informational purposes only; and

(5) Analysis of Sites 1 and 2 combined demonstrated strong evidence of a decrease in dioxin concentration over the seven year study, and a statistically significant decrease in dioxin concentration during the past four years. The statistical analysis of both Sites 1 and 2 combined demonstrated 94% confidence that there is a decrease in dioxin levels in fish taken from both sampling sites over the past seven years. The analysis of both Sites combined demonstrated a better than 99% confidence level that there is a statistically significant decrease in dioxin in fish taken from both sampling sites over the past four years. For the reasons stated in item (3) above, this conclusion is included for informational purposes only.

Discussion

At this point in time, the criteria in the Order relevant to determine whether the sampling program may be extended for yet another year is the trend for dioxin assays in fish fillets taken from Site 1. A statistically significant decline in assays at Site 1 would terminate the sampling and analysis program. As shown above, the statistical analysis has shown a decline in the dioxin levels at Site 1.

It is more indicative of the success of the remedial effort to consider the sampling results obtained after remedial activities commenced at Verona and after the presumed source(s) of dioxin contamination was removed. Using the four years of 1987-1990, a statistically significant decline in dioxin levels in fish taken from Site 1 is demonstrated to a confidence level greater that 99% using linear regression and to a confidence level of 98% using the Jonckheere test. This dramatically demonstrates that levels of dioxin in the fish have declined since the remedial efforts were initiated.

The criteria under the Order for extending the program considering Site 2 is whether there is a statistically significant aggregate increase in the fish results at Sites 2 through 5. This criteria has not been met as documented by the five year Final Progress Report and by the statistical report and analysis for the sixth year of the program. The dioxin levels detected in fish taken from Site 2 during this seventh year are the lowest ever recorded. Thus, the data for Site 2 do not justify an extension of the sampling program. (It is interesting to note that the analysis of Site 2 data demonstrated a statistically significant decrease in dioxin levels over the past four years.)

Finally, the data from both sites combined for the past four year period exhibited a statistically significant decrease in dioxin levels.

Because of the statistically significant decreases in dioxin levels during the past four years at Site 1, as discussed in the 1990 statistical analysis; and because of the lack of statistically significant increases in dioxin levels at Sites 2 through 5, as discussed in the Final Progress Report and the statistical analysis for the sixth year of the study; and in consideration of the sediment data reported in the Final Progress Report, further sampling and analysis under the Order and Plan is not warranted. In addition to the statistical information, an extension of the program is not called for in light of the extremely low levels of dioxin that have been detected during the course of the seven year study. The discussion of this observation in prior reports to EPA under the Order and Plan is underscored by the fact that the dioxin results obtained in this latest year of the study are the lowest levels ever recorded by the study.

Therefore, in consideration of the statistical analysis and of the extremely low levels of dioxin detected, particularly in this most recent year of the study, Syntex respectfully requests that EPA agree to the termination of the sampling and analysis program under the Order and Plan.

3127Q

STATISTICAL ANALYSIS OF DIOXIN DATA FROM SPRING RIVER

STATISTICAL PACKAGE

REPORT PREPARED BY: Shan-Shan Chen, MPH
Johanna S. Hunt, MStat

BIOSTATISTICIAN: Shan-Shan Chen, MPH

BIOANALYST: Michal Ben-Shachar, M.S.

Institute for Research Data Management
Syntex Research
Palo Alto, California

November 12, 1990

TABLE OF CONTENTS

I. STATISTICAL RESULTS

The dioxin concentrations in fish at the 0.3 mile location downstream from the confluence of the Slough Area and the Spring River were tested for a decrease over time using both a Jonckheere test and a Student's t test. The resulting p-values were 0.15 and 0.07, respectively, showing evidence of a decreasing trend over time. The same tests were conducted on data from site 2 (3.0 miles downstream) resulting in corresponding p-values of 0.43 and 0.26. The results of the two Jonckheere tests yielded a combined p-value of 0.24.

The data from both sites combined were then examined for a decrease over time using multiple linear regression methodology. The 90% confidence interval for the slope over time was (-0.102, 0.004) and the corresponding p-value was 0.06. This analysis also showed strong evidence of a decrease in concentration over the seven sampling years.

The alternative hypothesis tested by the Jonckheere test is that of a monotonic decrease, while the t test detects an overall decreasing trend. The result of the Jonckheere test is more influenced by an apparent increase at any one year, even if it is a function of the assay technique rather than a reflection of a real increase in concentration. In order to examine a more homogeneous set of data, a supplementary

analysis was conducted. All of the above tests were repeated using the data from only the last four years (1987 - 1990). In spite of decreased power due to the smaller sample size, the results indicated a highly significant decrease in dioxin concentrations over the past four years. The only p-value which was not less than 0.05 was that of the Jonckheere test at site 2 ($p = 0.10$). The p-values from the t tests at sites 1 and 2 were 0.007 and 0.03, respectively. The 90% confidence interval for the slope of sampling year was (-0.373, -0.147).

II. STATISTICAL METHODS

General Comments

This report includes the results of statistical analysis of dioxin concentrations in fish sampled at sites 1 and 2 during the years 1984-1990.

All tests were one-sided at a 0.05 significance level. A ninety percent confidence interval for the slope over sampling year was constructed from multiple linear regression. The regression analyses were performed using Release 6.06 of SAS (Statistical Analysis System); and the Jonckheere tests were performed using in-house software written in SAS Version 5.16.

Independent Data Points

One sample was assayed twice. Measurements from the same sample are not independent. To preserve the independence of the data points for statistical analyses, the mean value of the data points measured from the same sample was calculated and assigned to the corresponding sample.

Jonckheere Test

This nonparametric method[1] tested the following ordered alternative at sites 1 and 2:

Ha: C1984 > = C1985 > = C1986 > = C1987 > = C1988 > = C1989 > = C1990

where one of the inequalities must be strict and "Cyear" was the dioxin concentration in a specific year. For each pair of sampling years, this test compared all the possible combinations of two data points from different years and assigned scores as:

1	if Ci > Cj
1/2	if Ci = Cj
0	if Ci < Cj

Since there were two data points in each of the seven sampling years, there were 4 comparisons for each pair of sampling years, and 21 pairs of sampling years. Therefore, the Jonckheere statistic at each site was distributed from 0 to 84. The approximate one-sided alpha-level was calculated using an asymptotic normal distribution method. A corresponding test at each site was conducted on data from the last four years only.

Combined p-Value from Jonckheere Tests

The p-values calculated from Jonckheere tests of data collected at sites 1 and 2 were combined into one p-value using Fisher's method.[2] The chi-squared distribution has the property that (1) a chi-squared statistic having df = d > 1 can be partitioned into several independent chi-squared components, and conversely (2) several independent Chi-squared statistics can be combined into a chi-squared statistic.

The absolute value of twice the natural logarithm of a p-value is distributed as a chi-square with 2 degrees of freedom. Since data from the sites were independent, adding these two chi-squared statistics resulted in a statistic with a chi-squared distribution and 4 degrees of freedom. The corresponding p-value was the combined p-value for the two sites.

Least Squares Linear Regression

The least squares linear regression[3] model was examined using the SAS (Statistical Analysis System) procedure GLM for data collected at sites 1 and 2 separately. The model statement was of the form:

```
MODEL LOGCONC = YEAR
```

where

LOGCONC was the log transformed dioxin concentration, and YEAR was a continuous variable indicating seven (or four) sampling years. From this linear regression analysis, a one-sided t-test was used to test whether the coefficient of sampling YEAR was less than zero (decreasing).

Multiple Linear Regression

The multiple linear regression[3] model was examined using SAS (Statistical Analysis System) procedure GLM for data collected at sites 1 and 2 combined. The model statement was of the form:

```
MODEL LOGCONC = YEAR DISTANCE
```

where

LOGCONC was the log transformed dioxin concentration, YEAR was a continuous variable indicating seven (or four) sampling years, and DISTANCE was a continuous variable indicating the distance from the facility at two sampling locations. From this linear regression analysis, a 90% confidence interval was constructed for the slope over sampling year. This slope was also tested for a decrease using a one-sided t-test.

REFERENCES

1. Hollander, M. and Wolfe, D. (1973). Nonparametric Statistical Methods. John Wiley and Sons.

2. Fisher, R.A. (1958). Statistical Methods for Research Workers. Oliver and Boyd.

3. Draper, N.L. and Smith, H. (1966). Applied Regression Analysis. John Wiley and Sons.

ug/dioxin1990.jsh

III. TABLE

1. Dioxin Concentration (pptr) in Fish

SPRING RIVER, MISSOURI

TABLE 1

DIOXIN CONCENTRATION (pptr) IN FISH

LOCATION (MILES DOWNSTREAM FROM THE FACILITY)	DIOXIN CONCENTRATION (pptr) SAMPLING YEAR							ONE-TAILED P-VALUE*	
	1984	1985	1986	1987	1988	1989	1990	JONCKHEERE TEST	T-TEST
1 (0.3)	4, 4	4.5, 3.0	2.8, 2.5	6.5, 4.8	3.0, 3.2	4.7, 3.3	1.6/1.8, 2.1	0.15 (0.02)	0.07 (0.007)
2 (3.0)	3, 4	3.0, 3.0	2.3, 4.4	4.0, 3.4	4.2, 5.9	3.5, 4.1	1.9, 2.0	0.43 (0.10)	0.26 (0.03)

MULTIPLE LINEAR REGRESSION ANALYSIS OF LOCATIONS 1-2:

* ONE-TAILED P-VALUE FROM T-TEST OF NEGATIVE COEFFICIENT OF SAMPLING YEAR P = 0.06 (<0.01)

* 90% CONFIDENCE INTERVAL FOR THE SLOPE OF SAMPLING YEAR CI = (-0.102,0.004) (CI = (-0.373,-0.147))

COMBINATION OF PROBABILITIES FROM JONCKHEERE TESTS OF SIGNIFICANCE AT LOCATIONS 1-2: P-VALUE = 0.24 (0.01)

NOTE: 1. AT THE SAME SITE AND YEAR, DATA FROM THE SAME SAMPLE ARE SEPARATED BY "/"; DATA FROM INDEPENDENT SAMPLES ARE SEPARATED BY ",".
2. FOR LINEAR REGRESSION ANALYSIS, NATURAL LOG TRANSFORMATION WAS APPLIED TO DIOXIN CONCENTRATION.
3. P-VALUE/CONFIDENCE INTERVAL IN PARENTHESES IS FROM THE CORRESPONDING ANALYSIS OF 4 YEARS OF DATA (1987-1990).

*ONE-TAILED P-VALUE FROM: 1. JONCKHEERE TEST OF DECREASING RANK ORDER OF DIOXIN CONCENTRATION, 2. T-TEST OF NEGATIVE COEFFICIENT FOR SAMPLING YEAR FROM LINEAR REGRESSION ANALYSIS.

SOURCE: IRDM RMBS EPAPLOT (11/5/90 10:56) MBS$1075 #JONCKEPA (11/9/90) SSC$4945 #PROB (11/9/90)
RMBS EPAPLOT2 (11/9/90 9:34)

ug/dioconsampyr.ssc

IV. FIGURES

1. Dioxin Concentration in Fish (Log Transformed Data) - Location 1

2. Dioxin Concentration in Fish (Log Transformed Data) - Location 2

3. Dioxin Concentration in Fish (Raw Data)

4. Residuals of Dioxin Concentration from Linear Regression: Location 1 - Fish Data

5. Residuals of Dioxin Concentration from Linear Regression: Location 2 - Fish Data

6. Dioxin Concentration in Fish (Log Transformed Data) - Locations 1 and 2

7. Residuals of Dioxin Concentration from Multiple Regression: Locations 1 and 2 - Fish Data

MEMO
20 November 1990

To: D. Robertson

From: J. Hunt

Subject: Graphs of Data for 1990 Dioxin Report

Please find attached seven plots of data to be appended to the statistical report sent to you earlier concerning dioxin concentrations in fish samples from the Spring River. You will also find a revised list of figures (page 9). It should replace the list currently included in the statistical report.

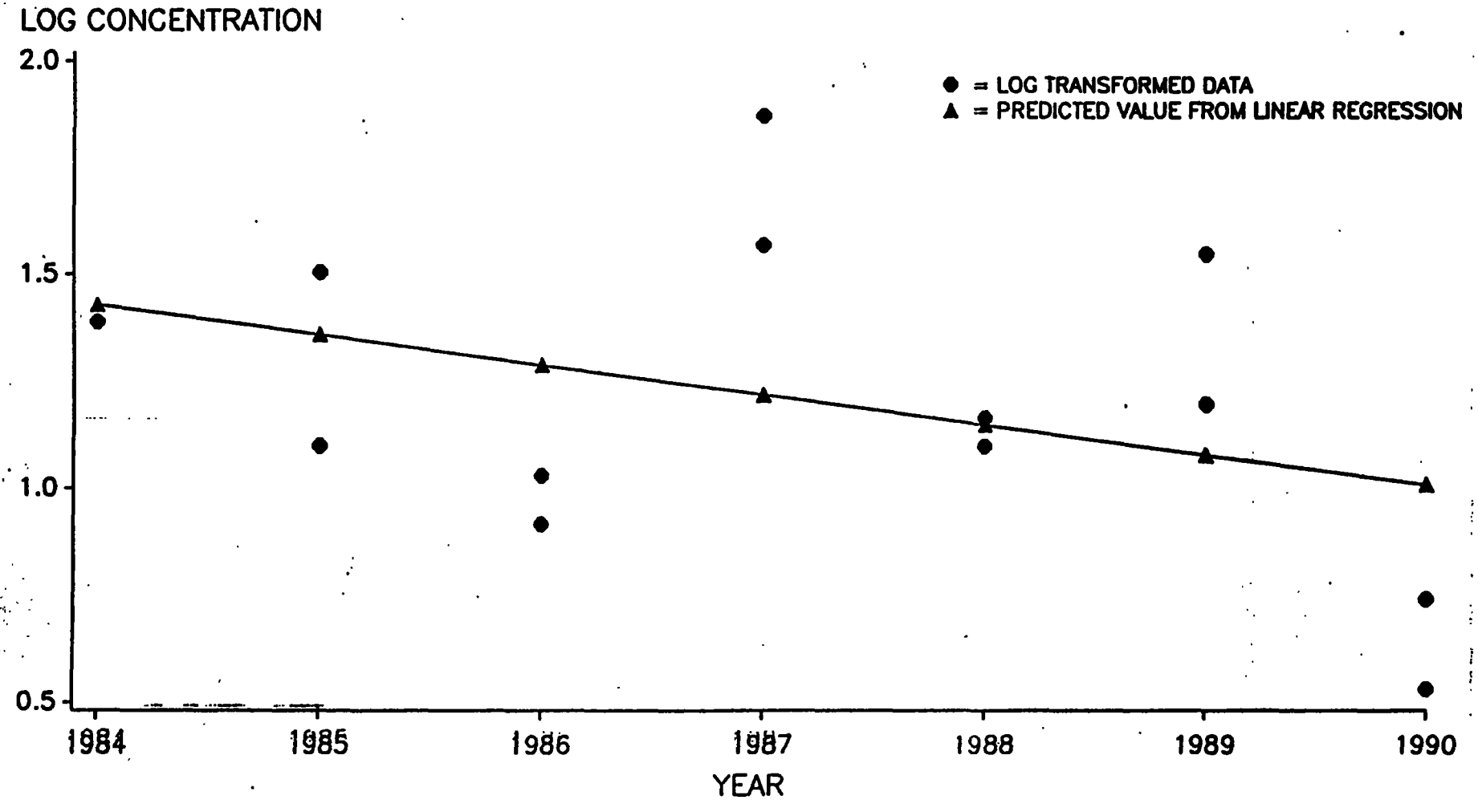
If I can be of any further assistance, please let me know.

SPRING RIVER, MISSOURI

FIGURE 1

DIOXIN CONCENTRATION IN FISH

LOG TRANSFORMED DATA -- LOCATION 1



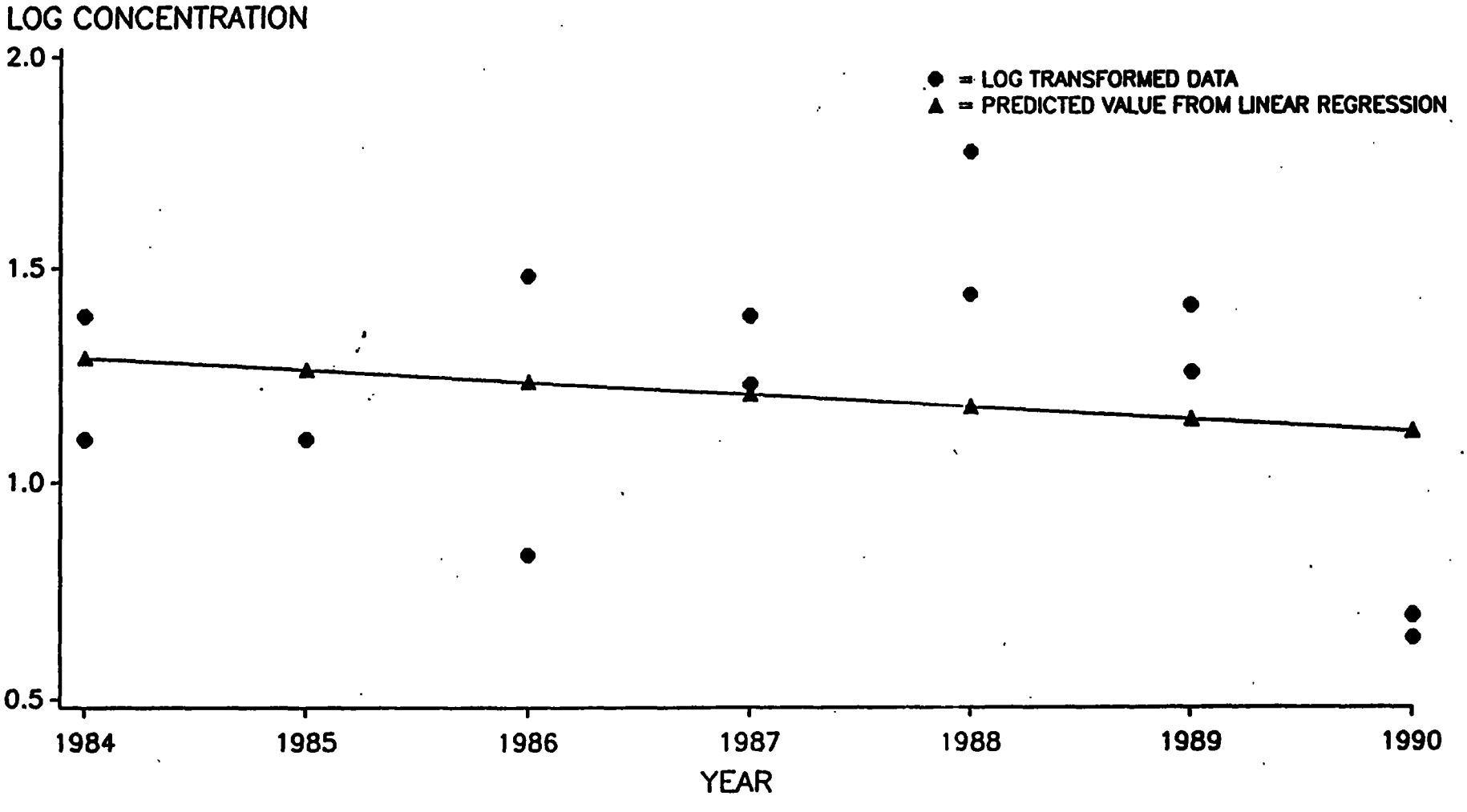
SOURCE: IRDM RMBS (05NOV90 10:55), RWMC PLOT1 (19NOV90 08:49)

SPRING RIVER, MISSOURI

FIGURE 2

DIOXIN CONCENTRATION IN FISH

LOG TRANSFORMED DATA -- LOCATION 2

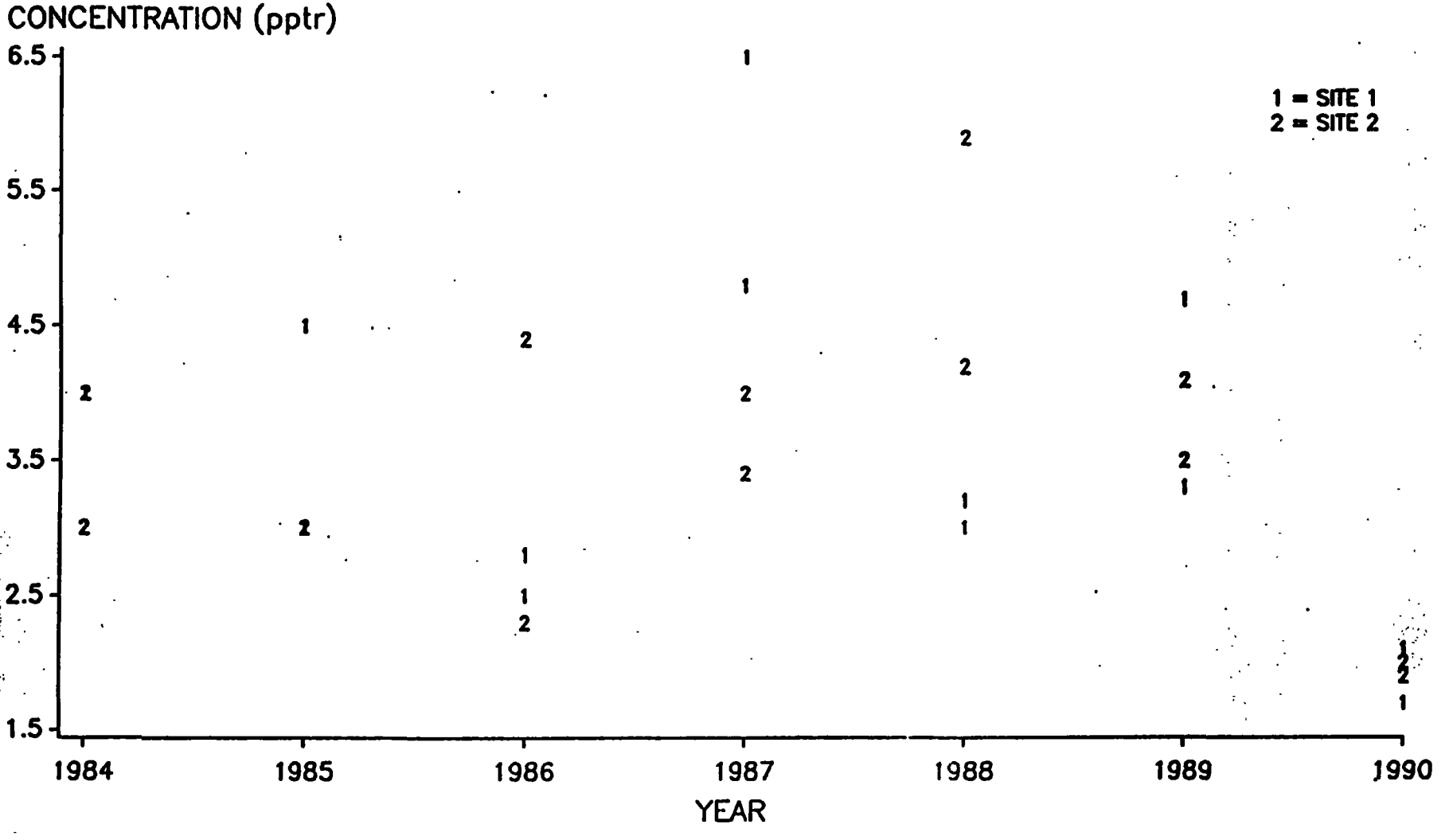


SOURCE: IRDM RMBS (05NOV90 10:55), RWMC PLOT1 (19NOV90 08:49)

SPRING RIVER, MISSOURI

FIGURE 3

DIOXIN CONCENTRATION IN FISH (RAW DATA)



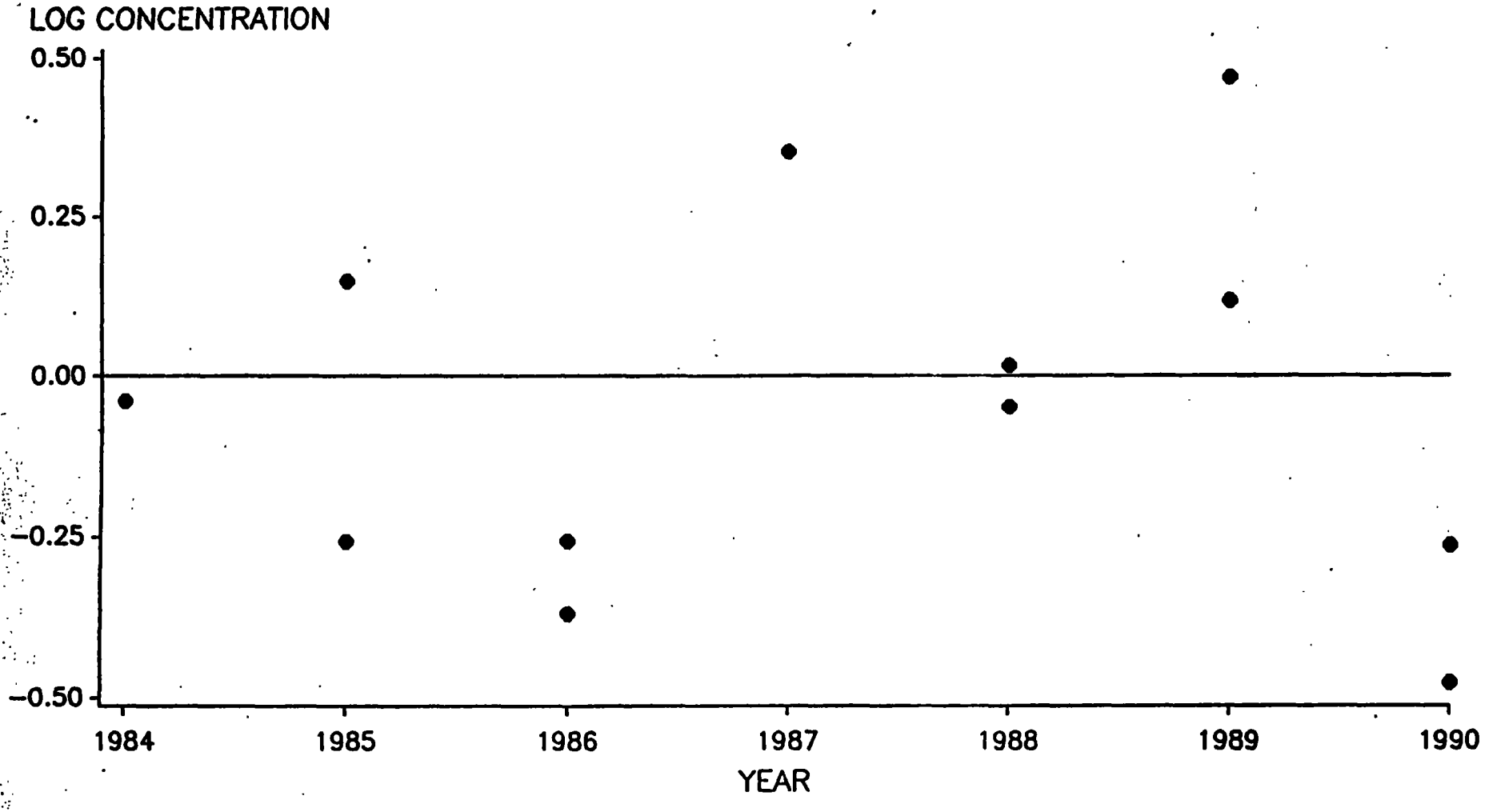
SOURCE: IRDM RMBS (05NOV90 10:55), RWMC PLOT3 (19NOV90 08:48)

SPRING RIVER, MISSOURI

FIGURE 4

RESIDUALS OF DIOXIN CONC. FROM LINEAR REGRESSIONS

LOCATION 1 -- FISH DATA



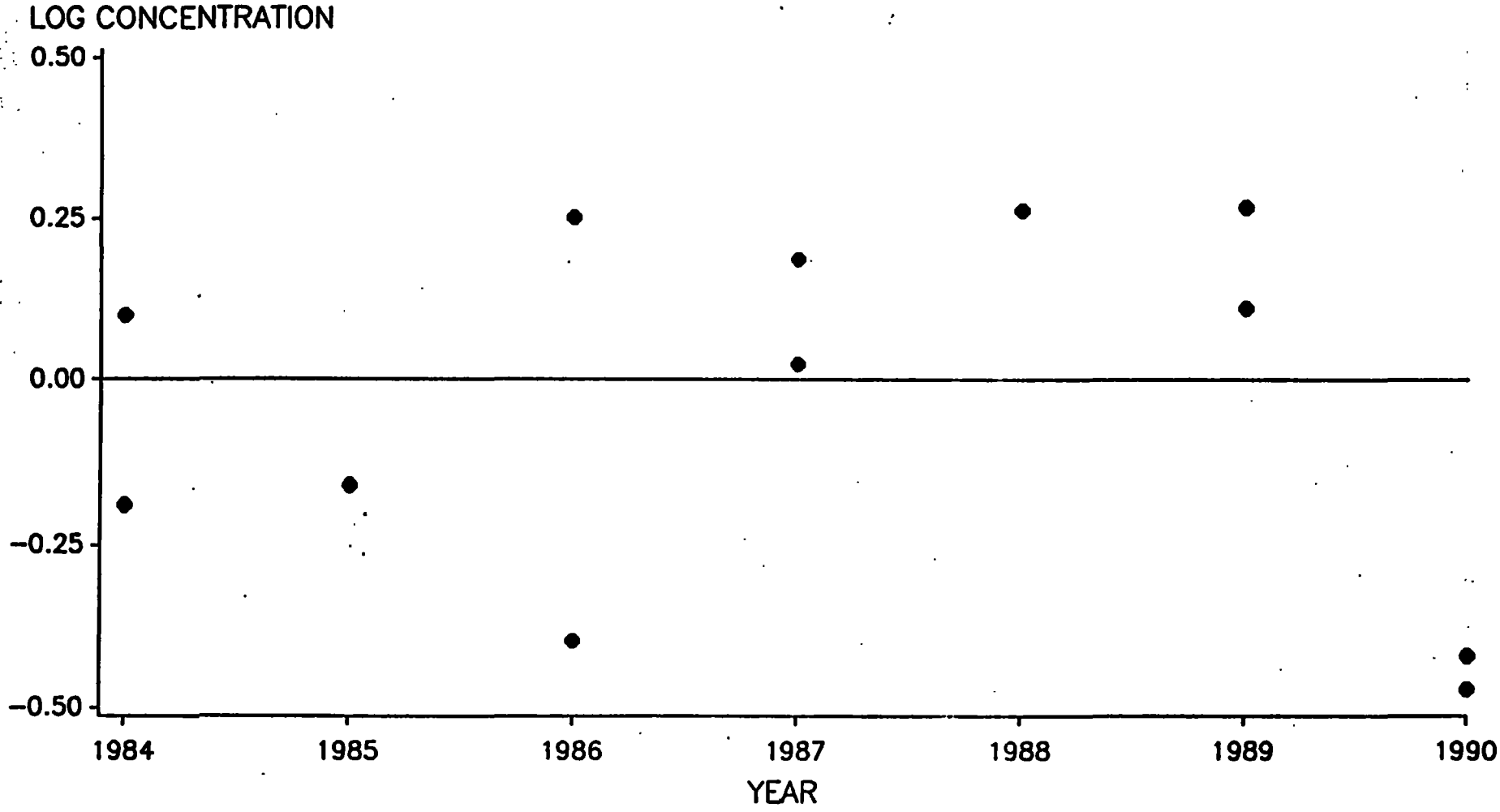
SOURCE: IRDM RMBS (05NOV90 10:55), RWMC PLOT4 (19NOV90 08:49)

SPRING RIVER, MISSOURI

FIGURE 5

RESIDUALS OF DIOXIN CONC. FROM LINEAR REGRESSIONS

LOCATION 2 -- FISH DATA



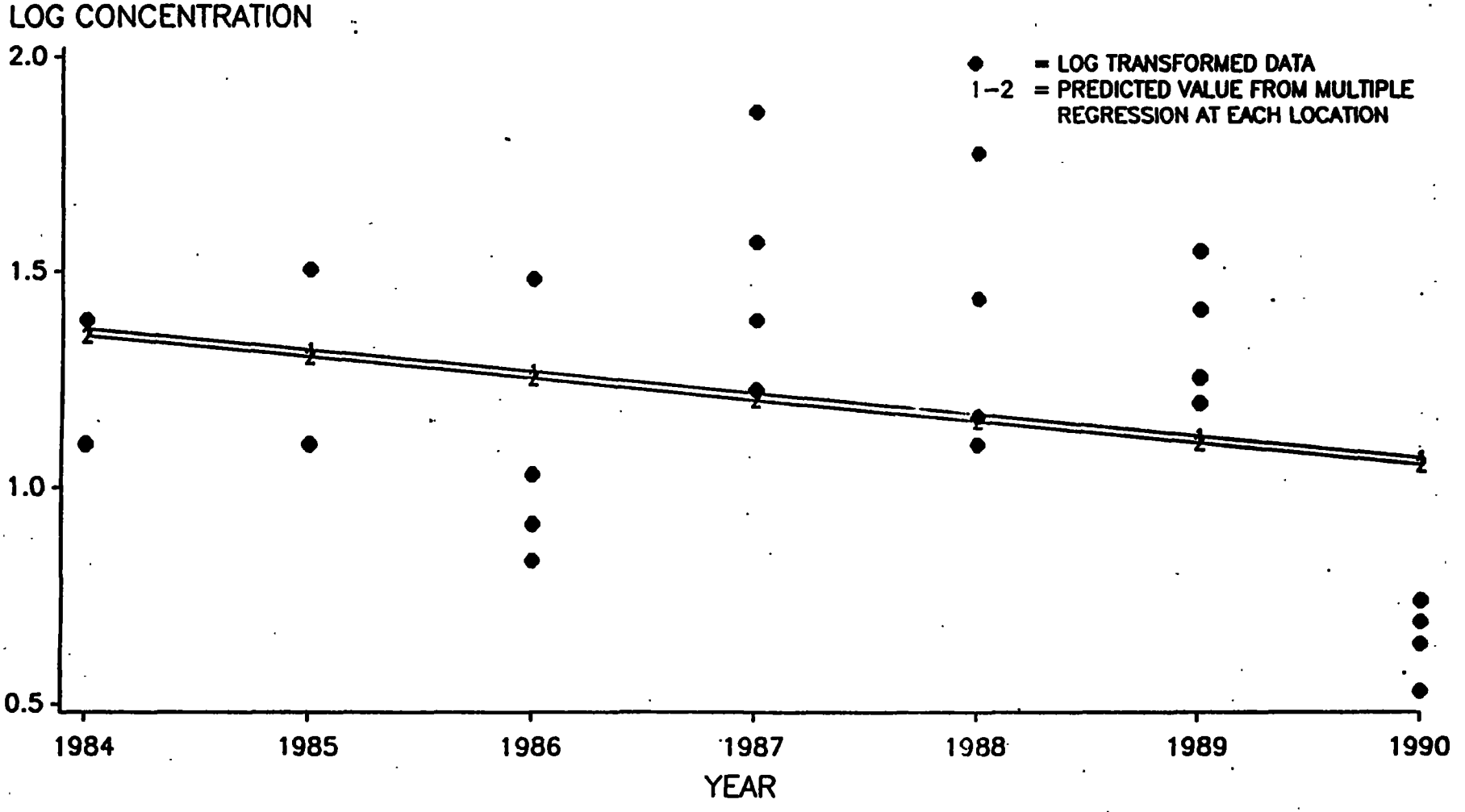
SOURCE: IRDM RMBS (05NOV90 10:55), RWMC PLOT4 (19NOV90 08:49)

SPRING RIVER, MISSOURI

FIGURE 6

DIOXIN CONCENTRATION IN FISH

LOG TRANSFORMED DATA -- LOCATIONS 1-2



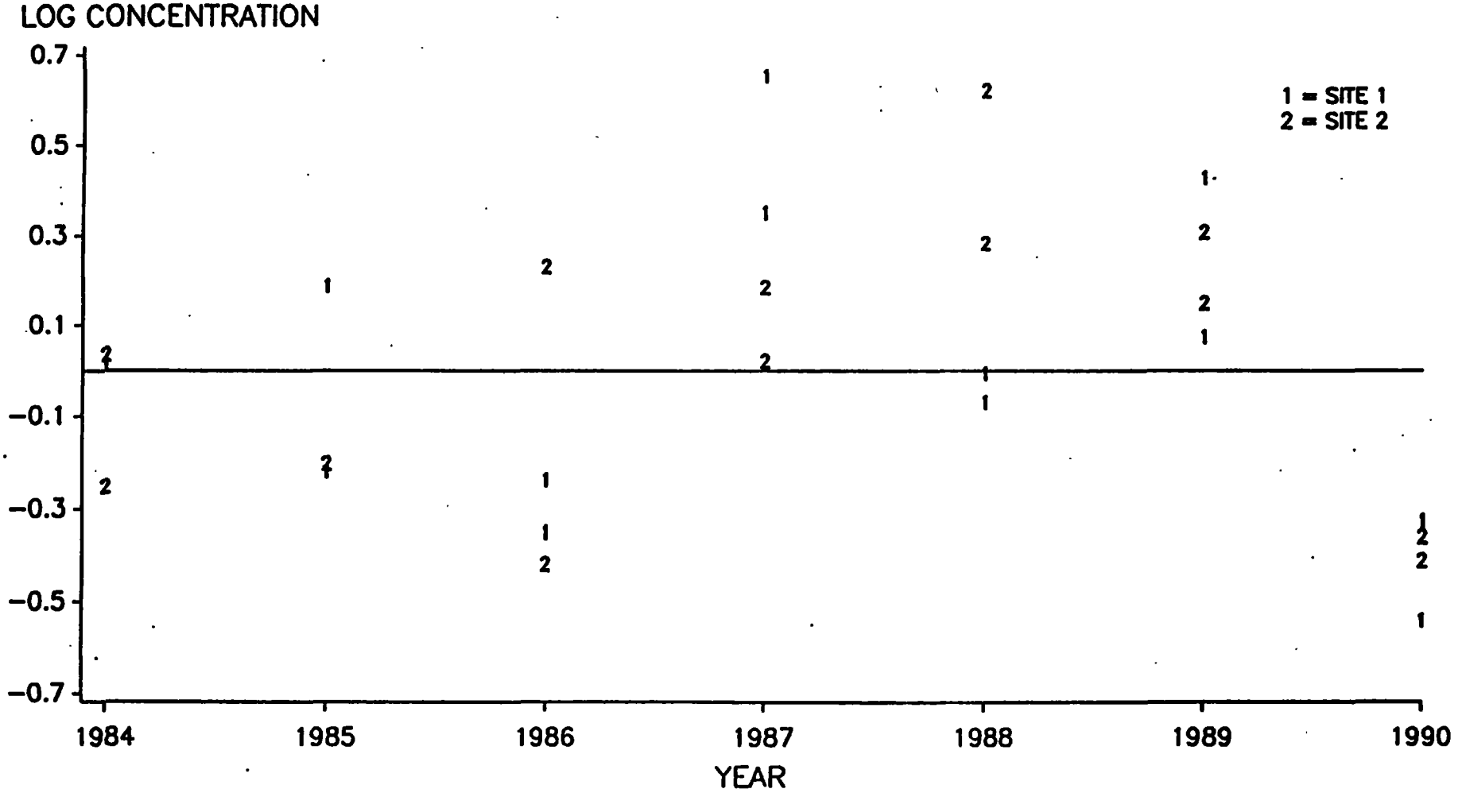
SOURCE: IRDM RMBS (05NOV90 10:55), RWMC PLOT6 (19NOV90 10:51)

SPRING RIVER, MISSOURI

FIGURE 7

RESIDUALS OF DIOXIN CONC. FROM MULTIPLE REGRESSION

LOCATIONS 1–2 -- FISH DATA



SOURCE: IRDM RMBS (05NOV90 10:55), RWMC PLOT7 (19NOV90 10:51)

ANALYTICAL AND ENVIRONMENTAL RESEARCH

MEMORANDUM

TO: D. Robertson (w/ attachments) AER: wp0423

FROM: K. Chan
B. Berridge

CC: K. Straub
L. Throop
L. Tokes

DATE: October 3, 1990

SUBJECT: Determination of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (2,3,7,8-TCDD) in Spring River Fish Collected in August, 1990.

This memorandum describes the results of the seventh year study of Verona fish. Levels of 2,3,7,8-TCDD in Catostomus commersoni (white suckers) collected from Verona's Spring River were determined using Syntex Method AR# 10,349 ("Determination of 2,3,7,8-TCDD in Fish by Capillary Gas Chromatography High Resolution Mass Spectrometry Using The Selected Ion Monitoring Technique (C-GC/HRMS-SIM)"). A summary of the results is shown in Table 1.

The fish were collected at only sites 1 and 2 of previous years (1984 - 1989) by the Missouri Department of Conservation (MDC) on August 7, 1990. The exact locations are described in the sampling records (Attachment 1). Subsequently, MDC and Environmental Trace Substances Research Laboratory prepared samples containing homogenate of fish fillets, remainders, and whole fish. Portions of each of these samples were packaged in polyethylene bags and were sent to Syntex for analysis. Syntex (c/o Dr. D. Robertson) received these samples from Ms. Cynthia S. Morris of MDC on September 11, 1990; the samples were frozen and in good condition upon arrival. At Syntex, these samples were stored frozen until just before the preparation for C-GC/HRMS-SIM analysis.

As previously agreed by Syntex and MDC, only the fillets were analyzed in this study. The samples were prepared for analysis by B. Berridge. 1.912 ng of ^{14}C labelled 2,3,7,8-TCDD was added to approximately 50 g of sample. The samples were saponified, extracted, and purified by column chromatography. Finally, the samples were reconstituted in 50 μl of toluene and submitted for C-GC/HRMS-SIM analysis.

These analyses were carried out by K. Chan using a Finnigan-MAT 8230 mass spectrometer directly coupled with a Varian 3700 gas chromatograph. Data were obtained using Finnigan SS300 version 6.01C software. Experimental conditions are shown with the raw data in the attachments. Areas of the chromatographic peaks were obtained and reported using SS300 programs "PAREA" and "PLIST". As in previous years, these data were then inserted to the "TCDD Report Program" (written by B. Brunck, last revision February 11, 1988) which was executed on an IBM PC to perform linear regression analysis on the calibration curves, to calculate the amount of 2,3,7,8-TCDD in the fish samples, and to generate reports as shown in the attachments.

As quality control, a standard addition experiment was carried out. 0.320 ng of 2,3,7,8-TCDD was added to 47.3 g of fillet of group B fish collected at site 2 (sample I.D. MDC90-7S). Analysis of this spiked sample showed a concentration of 8.8 ppt 2,3,7,8-TCDD, which is identical to the expected value (2.0 ppt + 6.8 ppt spike).

The above results show that the concentration of 2,3,7,8-TCDD in the fish samples collected from Spring River this year is slightly lower than the levels detected in 1989.

Attachments: 1. Sampling Records.
2. Documentation of TCDD Standards.
3. Raw data and "TCDD Reports".

TABLE 1

Concentration (in parts per trillion, ppt) of 2,3,7,8-TCDD in Catostomus commersoni Collected From the Verona Spring River in 1990.

Sample I.D.	Site-Group	Type	Results (ppt)
MDC90-1	1-A	Fillet	1.6/1.8[1]
MDC90-2	1-B	Fillet	2.1
MDC90-6	2-A	Fillet	1.9
MDC90-7	2-B	Fillet	2.0

1. Duplicate sample preparation and analysis.

A1-1

September 7, 1990

Mr. Robert Morby
Region VII
U.S. Environmental Protection Agency
726 Minnesota Avenue
Kansas City, Kansas 55101

Dear Mr. Morby:

On August 7, 1990 white suckers (Catostomus commersoni) were collected from two locations on the upper Spring River for TCDD analysis. This is in compliance with the seventh year of a continuing requirement outlined in the revised Verona Fish and Sediment Sampling Plan. The fish were collected by electroshocking and a representative from Syntex was present during sampling. The two sites correspond to those identified in the "Verona Plant, Fish and Sediment Plan". Site 5 was dropped in 1989 and sites 3 and 4 were dropped in 1990. These sites were identical to those sampled in August of 1984, 1985, 1986, 1987, 1988 and 1989. The sampling locations are identified in Attachment A. The size and weight of each fish and the identifying number is listed in Attachment B. The recommended minimum numbers of fish were met at all locations.

The fish were taken to our facility at Columbia, Missouri, thawed and prepared accordingly. The fish at site 2 were weighed and measured and sequentially placed into two equal size groups designated as Groups A and B. The right skinless fillets of the fish in Groups A and B were removed and placed in separate polyethylene bags. These two groups are to be analyzed separately. The remainder of Group B fish (the entire fish minus the right fillet) was placed in a third bag for analysis. A fourth whole body estimate will be calculated. The fish at Site 1 were prepared in a similar manner except they were sorted into three equal size groups. Group A and B were prepared in a manner identical to site 2 and the fish in Group C were simply left whole and refrozen. Thus a total of seven composites were prepared which will generate nine measurements (two calculated).

The frozen fish samples were delivered to the Environmental Trace Substances Research Laboratory in Columbia, thoroughly homogenized, a maximum of 100-gram samples were removed, refrozen, and delivered to Dr. David Robertson, Syntex Research, Palo Alto, California by Federal Express on September 10, 1990.

Sincerely,

Cynthia S. Morris
Fisheries Environmental Specialist

Enclosure

bcc: Stan Michaelson Alan Buchanan Glen Curtis
Steve Weithman David Robertson

A1-2